CHAPTER 10

Nano-Chemistry: an Introduction

10.1 Introduction to carbon nanotube

A new form of carbon graphitic tubules, also known as carbon nanotubes were first synthesized in 1991 by Iijima, after the discovery of fullerenes [225]. On each tube on the carbon-atom hexagons are arranged in a helical fashion. There are two main types of carbon nanotubes that can have high structural perfection [226]. First carbon nanotubes described by Iijima, had walls built from two to fifty graphene sheets [225], and were named as multi-walled carbon nanotubes (MWNTs). Single-walled nanotubes (SWNTs) were discovered thereafter which consist of a single graphite sheet seamlessly rolled into a cylindrical tube. MWNTs comprise an array of such nanotubes that are concentrically nested like rings of a tree trunk [226]. SWNT is a semiconductor with zero band gap, can be either metallic or semiconducting, depending role-up vector or 'chirality' of the SWNT [226]. The role-up vector in the graphite sheet and the nanotube diameter are accessible from a pair of integers (n, m) that denote the nanotube type (*1*)[226]. The nanotube is either of the armchair ($n = m$), zigzag ($n = 0$ or $m = 0$), or chiral (any other n and m) variety depending on the appearance of a belt of carbon bonds around the nanotube diameter [226]. All armchair SWNTs are metals while others are semiconductors with a tiny band gap [226].

Carbon nanotubes including SWNTs and MWNTs with exceptional structural, mechanical, optical and electronic properties have received much interest in potential applications including conductive and high-strength composites; energy storage and energy conversion devices; sensors; field emission displays and radiation sources; hydrogen storage media; and nanometer-sized semiconductor devices, probes, and interconnects [226]. However some of the major drawbacks for pristine carbon nanotubes are aggregation into bundles of different diameters due to the strong van der Waals attraction between individual hydrophobic nanotubes, insoluble in common solvents

and have poor dispersibility [227]. This has limited the applications of SWNTs, and necessitates the use of intricate processing.

10.2 Carbon nanotube functionalization

Solubility issues of carbon nanotubes can be overcome using various methods of surface modification. Several approaches to the functionalization of SWNTs have been developed, in both molecular and supramolecular chemistry. These approaches include defect functionalization, covalent functionalization of the sidewalls, noncovalent exohedral functionalization (formation of supramolecular adducts with surfactants or polymers) and endohedral functionalization [227]. Such methods can also render the SWNTs soluble in water, which is important in biosensors and drug delivery systems.

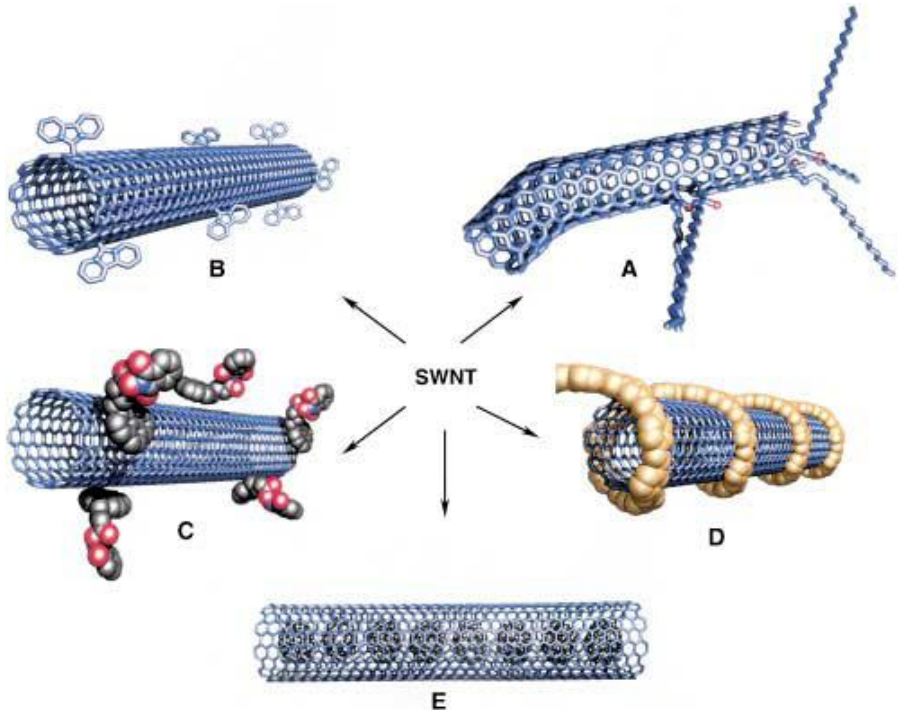

Figure 10.1. Various functionalization for SWNTs: (A) defect-group functionalization, B) covalent sidewall functionalization, C) noncovalent exohedral functionalization with surfactants, D) noncovalent exohedral functionalization with polymers, and E) endohedral functionalization [227].

Defect functionalization can be achieved via “end and defect-side chemistry” [227, 228]. Purifications of SWNTs involve the removal of metal particles or amorphous carbon from the crude material by oxidative methods using concentrated acids. Under the harsh conditions, defects in the sidewalls and open ends are usually present in the nanotubes[227]. These defects become the potential site for further chemical modification for reactive groups such as carboxylic groups [227]. Consequently amidation of carbon nanotubes can be performed on the carboxyl-functionalized nanotubes by first substituting a hydroxyl (–OH) group in a carboxylic (–COOH) group on chlorine by treatment in $SOCl_2$ with the following addition of a long chain molecule of octadecylamine which has been reported by Haddon [229]. Functional groups such as -COOH, -NO_2, OH, H, and =O are always present on the terminal of the carbon nanotubes [227]. Other covalent functionalization is the direct sidewall functionalization of SWNTs with reactive species such as nitrenes, carbenes, and radicals [227, 230-232]. For example, the thermal reaction of azidoformiates leads to N_2 extrusion and to aziridino-SWNTs, which dissolve in organic solvents to give black solutions [231, 232]. Fluorination of nanotubes can achieve higher degree of functionalization and allows further modification of nanotubes by replacing fluorine with other functional groups similar to carboxylation [233-235].

Another class of nanotubes functionalization is the noncovalent exohedral functionalization, which involves the formation of noncovalent aggregates with surfactants or wrapping nanotubes with polymers or peptides [227]. The advantage of this functionalization method is that it does not destroy the electronic structure of the nanotubes. Nanotubes can be dispersed to the aqueous phase in the presence of surface-active molecules such as sodium dodecylsulfate or benzylalkonium chloride in which the nanotubes are in the hydrophobic interiors of the corresponding micelles resulting in stable dispersions [227, 236-238]. When the hydrophobic part of the amphiphile contains an

aromatic group such as N-succinimidyl-1-pyrenebutanoate, affords strong interaction from the effective π-π-stacking with the graphitic sidewalls of the SWNTs and the forms aggregation. In these aggregates, the succinimidyl group can be substituted with amino groups from proteins such as ferritin or streptavidin, which caused immobilization of the biopolymers on the tubes [227,239].

The formation of supramolecular complexes of SWNTs in the presence of polymers such as poly(*m*-phenylene-*co*-2,5-dioctoxy-*p*-phenylenevinylene) affords the suspension of nanotubes in organic solvents with the polymer wrapping around the tubes, while the wrapping of SWNTs with polymers that bear polar side-chains, such as polyvinylpyrrolidone or polystyrenesulfonate, leads to stable solutions of the corresponding SWNT/polymer. It is noteworthy that the bundles are mostly broken up on complex formation [227, 240-244].

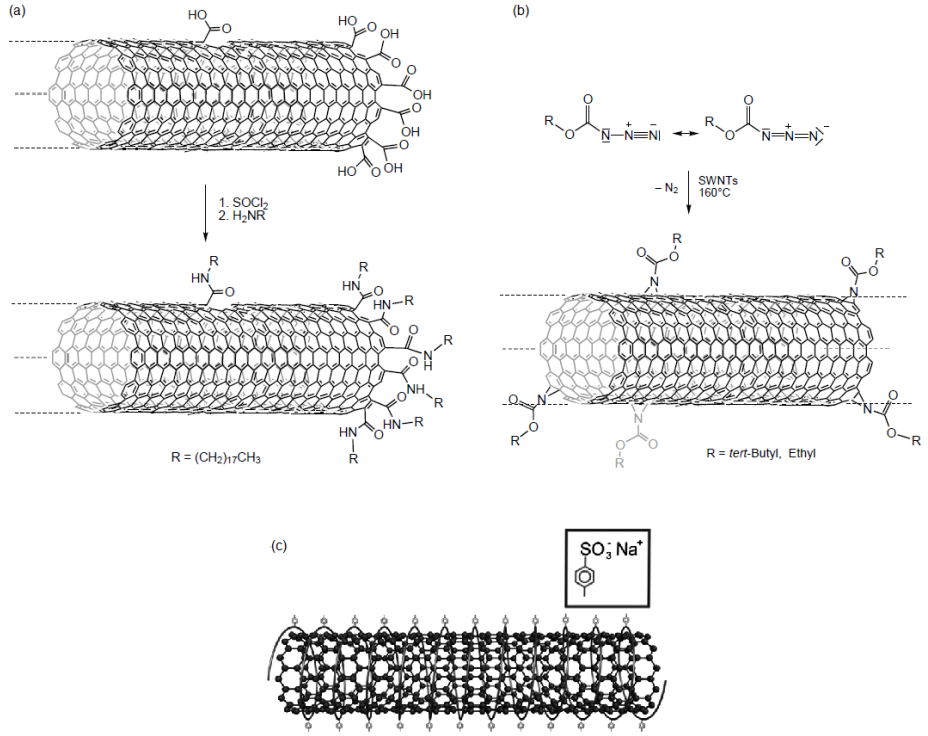

Figure 10.2. (a) Defect-group functionalization of SWNTs with octadecylamine, (b) sidewall functionalization of SWNTs with alkyl azidoformiates and (c) hydrophilic SWNTs prepared by wrapping of the water–soluble poly (sodium 4-styrene sulfonate) around SWNTs [275, 242].

10.3 Carbon nanotubes and calixarenes

There have been restricted studies on the use of water-soluble calixarenes for the solubilization of SWNTs. Lobach *et al.* [245] reported different types of amphiphilic macrocycles, bearing different upper and lower rim functionalized calix[4]resorcinarene and *p*-sulfonatocalix[n]arenes (n = 4, 6), modified by lower rim alkyl substituents (butyl and dodecyl), with the ability to form stable suspensions of SWNTs in aqueous media. Ogoshi *et al.* [246] investigated the carbon nanotube complexation with *p*-sulfonatocalix[n]arenes (n = 4, 6, 8) and found that solubilization of SWNTs is successful with the higher order oligomers, wherein *p*-sulfonatocalix[8]arene forms a dimer as part of a supramolecular SWNT network polymer. Hubble *et al*. [247] recently reported the effective solubilization and stabilization of SWNTs in aqueous media using the water-soluble *p*-phosphonated calixarenes and analogous compounds of differing lower rim functionality as well as extended arm' *p*-sulfonated calix[8]arene. The findings include a preferential solubilization of specific diameter SWNTs and subsequent preferential enrichment of SWNTs with semiconducting or metallic electronic properties which is of interest for the possibility of creating different SWNT-calixarene arrays to facilitate the separation or purification of the SWNTs in aqueous media. *p*-Phosphonic acid calix[4]arene modified by butyl substituents on the lower rim shows the ability to preferentially bind to 1.04 nm diameter metallic SWNTs, while *p*-benzyl-sulfonatocalix[8]arene and *p*-phenyl-sulfonatocalix[8]arene solubilized larger SWNT diameters (1.55 and 1.42 nm). In addition, *p*-phosphonic acid calix[6]arenes only solubilized 0.89 nm semiconducting SWNTs.

10.4 Introduction to fullerenes

The discovery of fullerenes in 1985 represents one of the striking and appealing breakthrough in chemistry and earned the 1996 Nobel Prize in chemistry for Robert F. Curl and Richard E. Smalley from Rice University, Houston USA and Harold W. Kroto from the University of Sussex, UK for their work in this area [2]. Fullerenes such as C_{60} and C_{70}, are three dimensional closed-cage molecules solely made up of carbon in the sp^2-hibridized state and constituting the third form of carbon (after diamond and graphite). Each fullerene C_n consists of 12 pentagonal rings and any number of hexagonal rings, m, such that $m = (C_n - 20)/2$ (Euler's theorem) [248]. For example, interlocking of 12 pentagons and 20 hexagons form the structure of C_{60}, a spherical 60-vertex solid (a truncated icosahedron) and the molecule has the exact structure as Kroto's stardome as well as a European football, and the geodesic domes of the architect R. Buckminster Fuller [2]. The molecule was named buckminsterfullerene thereafter. The closely related C_{70} is a cylindrical-shaped molecule with identical ends to C_{60} but with an extra row of hexagons about the middle [2]. Fullerenes have no hydrogen atoms or other groups attached, and are unable to undergo substitution reactions [248]. As the cages consist entirely of sp^2-hybridized carbons which have electron-withdrawing –I inductive effects, the fullerenes are strongly electron-attracting [246, 247]. This affects their chemical behaviour; for example they react readily with nucleophiles [248].

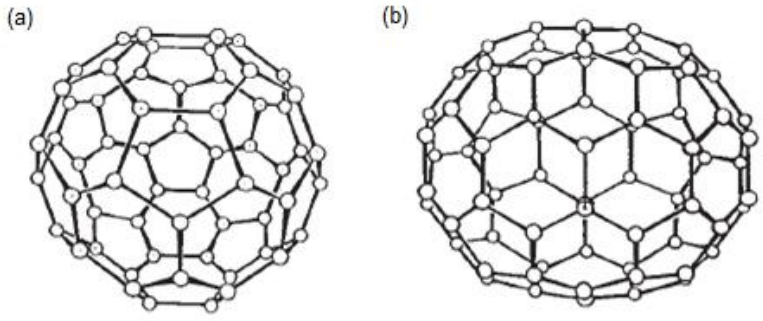

Figure 10.3. (a) Fullerene C_{60} and (b)fullerene C_{70} [246].

At room temperature the most abundant C_{60} and C_{70} species, with soccer and rugby ball shapes respectively, have been shown to crystallize as rotationally disordered molecules in either a face centered cubic (fcc) structure or a hexagonal closed packed (hcp) form [250]. The fcc structure is preferred for C_{60}, although the hcp can be crystallized when there is a small amount of impurity [251]. However, the hcp packing is preferred for C_{70} when grown at room temperature, but the former fcc structure can be crystallized when the nucleating substrate is maintained at an elevated temperature [252].

Nevertheless, pristine fullerenes aggregate very easily becoming insoluble or only sparingly soluble in many common organic solvents. Most of the fullerene aggregation studies have focused on the behaviour of C_{60} with the earliest evidence of fullerene aggregate formation in solution was provided by studies of the temperature dependence of the solubility of C_{60}. Ruoff *et al.* [253] reported that the solubility of C_{60} in benzene, instead of increasing with temperature, peaked at ~280 K and then decreased over a narrow temperature range. Bezmelnitsin *et al.* [254] proposed that this behaviour can be explained from the formation of solute aggregates and proposed that dissolution of the aggregates above 280 K increases the concentration of free fullerene (monomer) that results in the decrease in solubility observed. Chu *et al.* [255] examined the aggregation of C_{60} in a room-temperature, benzene solution at concentrations near the solubility limit using scattering methods and found that aggregates can grow exponentially with time and could be destroyed by modest mechanical agitation of the solution. Several studies of C_{70} aggregates have also been reported. Ghosh *et al.* [256] observed the solvatochromic behaviour of C_{70} in a variety of binary solvent mixtures by optical absorption, fluorescence, and light scattering techniques and concluded that stable aggregates were formed ranging in size from ~100 to ~1000 nm. Sun and Bunker [257] reported a marked change in the absorption spectrum of C_{70} that they attributed to

aggregate formation in binary solutions of toluene with varying concentrations of acetonitrile.

10.5 Water soluble fullerenes

Fullerene and fullerene derivatives feature in multidisciplinary research in the area of materials applications. However, the very low solubility of fullerenes in aqueous solvents is a major difficulty deterring their application in clinical practice.

Stable solutions of dispersed fullerene in water without any stabilizer is achievable with the introduction of solvents and was first introduced by Scrivens *et al.* [258] by dissolving C_{60} in a series of solvents, starting with benzene, THF, acetone and finally water. Stable dispersions of fullerenes in water can also be achieved by using binary solvent, i.e. THF and water. Ko *et al.* [258, 259] reported the preparation of water-soluble fullerenes, C_{60} and C_{70} by applying ultrasonication to the material with a mixture of concentrated sulfuric acid and nitric acid. Ultrasonic waves in liquids can cause chemical reactions either in homogeneous or in heterogeneous systems, promoted by cavitation or the formation of microbubbles in liquids caused by ultrasonic waves travelling in the liquid which generate high pressures and temperatures in their surroundings [261, 262].

Other approach in preparing water-soluble fullerenes is the fullerene surface modifications (or covalent functionalization), wherein suitable functional groups (hydrophilic, ionic and non-ionic) are attached on the aromatic molecule, introducing various derivatives of fullerene, such as carboxylic acid fullerene derivatives, amino acid fullerene derivatives, fullereneol, peptide and oligonucleotide functionalized fullerene derivatives, protein–fullerene conjugates, pendant fullerene polymers, main-chain fullerene polymers, and dendrimeric fullerenes [263]. Host-guest binding complexation also affords water-soluble fullerene, the method involves the inclusion of

C_{60} within water-soluble hosts such as cyclodextrins. Investigations on the noncovalent supramolecular complexation of fullerenes with water soluble cavitands, notably cyclodextrins have been developed. Samal *et al.* [264] reported complex of fullerene–β-cyclodextrin conjugates with the fullerene covalently linked to the cavitand. Inclusion of C_{60} in γ-cyclodextrin host was able to increase the solubility in water. Discrete 1:1 and 2:1 complexes with γ-cyclodextrin have been reported by Anderson *et al.* in 1992 [265] and the application of large cyclodextrin is possible to solubilise both C_{60} and C_{70} in water. Concentrations are only of the order of 10^{-4} giving a slight yellow colour to the solution in contrast to the deep reds and purples of fullerenes in aromatic solvents such as benzene and toluene. Modelling suggests that the five-fold axis of the fullerenes in orientated parallel to the pseudo-eight-fold-axis of the cyclodextrin [2].

Other preparation of water-soluble fullerene involves the assembly of fullerene with *bis*-β–cyclodextrin with a coordinated metal centre through end-to-end intermolecular inclusion complexation [266]. Supramolecular encapsulation of the aromatic molecule with macrocyclic calixarene has also been studied and Williams *et al.* first used water-soluble calixarenes derivatives to include C_{60} [267].

10.6 Fullerenes and calixarenes

Calix[n]arenes are polyphenolic molecules with hydrophobic cavities and have been shown to complex fullerenes which the phenomenon is driven by π-π interactions and/or solvophobic effects, while the complementarity of the curvature of the interacting species maximizes the number of intermolecular contacts [268]. Inclusion complexes obtained from various calixarenes have found applications for the direct purification of fullerenes from carbon soot [269, 270].

10.6.1 Fullerenes and calix[8]arenes

Atwood [269] and Shinkai [270] discovered independently that toluene solutions of C_{60} and *p*-tert-butylcalix[8]arene form a sparingly soluble brown–yellow precipitate which was identified as the 1:1 complex with the fullerene most likely resides within the cavity of the macrocycle resembling a "ball and socket" structure. The formation of this complex was anticipated based on the perfect complementarity between host cavity and guest size. However the stability of the supramolecular assembly was limited to the solid state and dissociation into each component was observed in solution. Is it noteworthy that the complexation with *p*-tert-butylcalix[8]arene is highly selective for C_{60} as opposed to higher fullerenes (C_{70}, C_{76}, C_{78}), thus this provides the basis for a convenient purification of C_{60} from the soluble fullerene soot extract [268]. The precipitation of the complex from toluene, followed by recrystallisation from $CHCl_3$, yields high-purity C_{60} while the calix[8]arene remains dissolved [268-270].

10.6.2 Fullerenes and calix[6]arenes

Atwood and co-workers [271] have demonstrated that calix[6]arene readily forms solid state complexes with C_{60} and C_{70} from toluene solutions resulting in crystallization of the well defined 1:2 stoichiometry complexes *p*-tert-butylcalix[6]arene · $(C_{60})_2$ and *p*-tert-butylcalix[6]arene · $(C_{70})_2$. The macrocyclic hosts show a double-cone conformation with an overall arrangement resembles the jaws of a pincer acting on two adjacent spheres/ellipsoids and each of the associated shallow cavities is occupied by a fullerene [268]. Treatment of the solid inclusion complexes with chloroform decomposes the products which gives the precipitates purified fullerenes and chloroform solvated calixarenes, stabilised by C-H···π interactions which are strengthened by the high acidity of the chloroform C-H group [266]. Shinkai and co-workers [272] also reported the preparation of inclusion complexes between C_{60} and the calix[6]arene derivatives

bearing electron rich *N*,*N*-dialkylaniline groups which are known to bind with C_{60} in organic solvents resulting from the strong donation ability of the *m*-phenylendiamine fragment [268].

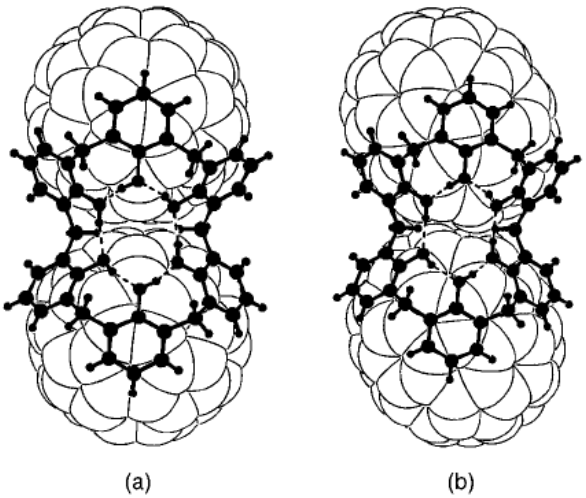

Figure 10.4. Structures of (a) [(calix[6]arene)$(C_{60})_2$] and (b)[(calix[6]arene)$(C_{70})_2$].[271]

Raston and co-workers [273] demonstrated that *p*-benzylcalix[6]arene, and C_{60} form a fullerene rich inclusion complex in toluene, $(C_{60})_3$(*p*-benzylcalix[6]arene)(toluene). The fullerene and toluene molecules shroud linear arrays of the calixarenes in the presence of methylene chloride to form an all carbon hcp polymorph of fullerene C_{60}. The structure of the C_{60}/*p*-benzylcalix[6]arene complex was found to be remarkable because fullerenes are not in the cavities, but rather the pendant arms of other calixarenes reside in the cavities as part of a continuous linear array of calixarenes.

10.6.3 Fullerenes and calix[5]arenes

Comprehensive investigations of the complexation of fullerenes with calix[5]arene receptors were carried out by Fukuzawa and co-workers [274]. Upon addition of calix[5]arene hosts to C_{60} in several organic solvents (toluene, CS_2, *o*-dichlorobenzene), changes were observed in the electronic spectra. A 1:1 stoichiometry of the complexes were formed in solution however the stoichiometry of the complex formed from calix[5]arene receptors bearing three methyl and two iodo substituents in the solid state was found to be 2:1 [268]. The fullerene is effectively encapsulated within a cavity conformed by two calixarene molecules. The apparent contradictory host-guest ratio in solution and in the solid state was observed in several other examples of fullerene-based supramolecular assemblies and it is quite reasonable to have a different complexation ratio in dilute solution to that in the solid state [268].

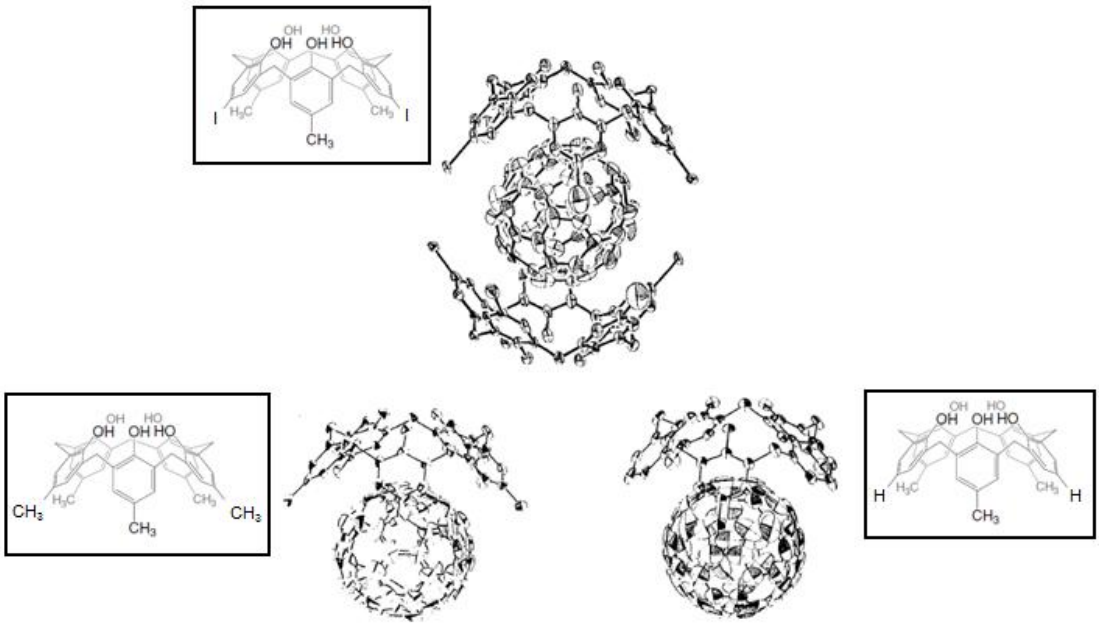

Figure 10.5. Structures of the supramolecular complexes of C_{60} with calix[5]arenes.[274]

Raston and co-workers demonstrated that C_{60} forms an intricate structure with calix[5]arene and toluene in a 5 : 4 : 2 ratio [275]. Addition of C_{70} to the solution influences the composition of the resulting crystals, yielding a 1 : 1 : 1 calix[5]arene : C_{60} : toluene complex in the solid state [276]. Despite an increase in the C_{70}/C_{60} ratio, and the superficial similarity in size and shape of the two fullerenes, C_{70} is not incorporated into the calix[5]arene/C_{60} structure [276]. When *p*-xylene was substituted for toluene, calix[5]arene and C_{70} form a ball-and-socket supramolecular 1:1 complex with with the *C*5 axis of the fullerene tilted 40° relative to the symmetry axis of the calixarene, the extended structure is comprised of well-separated zigzag sheets of C_{70} molecules [276]. Raston and co-workers [277] have also reported binding studies of C_{60} with *p*-benzylcalix[5]arene showing the formation of 2:1 complex with C_{60} in which the fullerene is shrouded by two staggered *trans* host molecules in the cone conformation with dangling benzyl groups and the symmetry axis of the calixarene is aligned with a *C*5 symmetry-element of C_{60} [277]. However, in the case of C_{60} complex of *p*-phenylcalix[5]arene, the rigid extended arms interdigitate in one hemisphere of the 2:1 supermolecule such that symmetry matching for both calixarenes is not possible, and the "confused" fullerene is now completely disordered. It appears that the presence of the benzyl units may play an important role as they can provide additional intramolecular π-π interactions between the two host macrocyles within the 2:1 complex[277].

10.6.4 Fullerenes and calix[4]arenes

Calix[4]arenes and calix[4]resorcinarenes have cavities that are relatively small to form inclusion complexes with fullerenes [268]. Despite the loss of a cavity allowing the formation of true inclusion compounds, co-crystallization of simple calix[4]arenes have been shown to form stable crystalline complexes with C_{60} with the fullerene *exo* to the

calixarene cavity, and include [278]: (i) *p*-phenyl-calix[4]arene, which has a toluene molecule in the cavity; the overall structure is dominated by fullerene–fullerene and *exo*-calixarene– fullerene interactions [279], (ii) *p*-bromo-calix[4]arene propyl ether with the structure shows very close interfullerene contacts in a columnar structure, which most likely results in opposing induced dipoles from the unidirectionally aligned calixarenes [280], and (iii) *p*-iodo-calix[4]arene benzyl ether resulted in a remarkably well packed structure in which the C_{60} molecules are intercalated into calixarene bilayers thus preventing appreciably strong interfullerene interactions [281]. Georghiou and co-workers [282, 283] have reported the complexation of the *endo*-type calix[4]naphthalene and its tetra-*t*-butylated derivative with C_{60} in various organic solvents [268]. There is also calix[4]resorcinarene which has a molecular capsule derived from head-to-head hydrogen bonding of two resorcinarene and propan-2-ol molecules wherein the fullerenes are arranged in columns [284]. *Bis*-calix[4]resorcinarene is effective in binding C_{60}, and calix[4]resorcinarenes that bear dithiocarbamate groups between the oxo groups, with R = alkyl chains and with methylene groups between adjacent oxo groups form torus-shaped complexes that comprise three calixarenes with divalent cadmium and zinc ions, which effectively bind C_{60} [278, 285, 286].